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RESEARCH ON MECHANISMS OF ALLOY STRENGTHENING

- ✓ I. Alloy Strengthening by Fine Oxide Particle Dispersions
✓ II. The Splat Cooling Process for Alloy Development

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I. ALLOY STRENGTHENING BY FINE OXIDE PARTICLE DISPERSIONS

A) Modes of Deformation and Fracture in Oxide Dispersed Metal Systems

Relatively large amounts of strip material, ranging in thickness from several thousandths of an inch to 1/8 inch, have been produced from a group of dilute copper alloys containing aluminum (up to 3.5 percent). The very thin sheets are being used to optimize the processing variables in internal oxidation. The thicker strip will be used for alloy production, mechanical testing, and X-ray and metallographic studies.

The temperature of 650°C appears to be optimum for the internal oxidation process. Micrographic studies at 500 and 1000X show a relatively uniform grain size for these alloys, varying by less than a factor of two from the strip surfaces to the center of the strip.

It was felt to be extremely important to avoid grain size variations in order to avoid or decrease the tendency for preferred oxide formation on the grain boundaries.

Electron microscopy studies have worked out well. By a two-stage carbon replication technique the resultant internally oxidized structures are indicated to be of quite uniform particle size and the oxide dispersion to be homogeneous. Particle size measurements show the aluminum oxide particles to vary between 110 and 190 Å in diameter, with interparticle spacings of the order of 800 Å. These values place us almost exactly where we had hoped to be.

Measurements of the rate of oxide penetration at these lower temperatures are in good agreement with the earlier results of Rhines and co-workers, and of Preston and Grant. Oxidation times are found to be reasonable and practical; penetration of oxide to a depth of .23 mm takes place in about 25 hours at 650°C.

Experiments with thinning techniques for transmission electron microscopy indicate the need for a three-step procedure. First, the strip is generally thinned by chemical etching in dilute nitric acid; this is followed by the window technique to thin down a local section; and finally, the Bollman technique of preferential etching of the center of the specimen is applied. For this purpose, an apparatus has been built which utilizes the Bollman technique. Some of the early transmission microscopy work appears to be extremely promising.

Mechanical property tests are continuing. Base line data are being obtained on the annealed and solution treated alloys; after internal oxidation but in the absence of cold work; and finally, for small but increasing amounts of cold rolling at room temperature after internal oxidation. The next report should be able to provide more extensive data on these tests.

Recrystallization studies of the cold rolled thin plates are under way. It is the intent of these recrystallization studies to produce coarse grained structures which will permit internal oxidation of selected or preferred areas: (a) of grains but not of grain boundaries;

(b) of grain boundaries but not of the total grain area; (c) of grains to produce one particle size (fine), and of grain boundaries to produce a second, coarser particle size. In this way, hopefully, the contributions of grain and grain boundary regions can be compared.

B) Oxide Dispersion Strengthened Iron - BeO Alloys

The extended studies carried out for over a year to establish the combination of treatments and processes to produce the best possible dispersion of BeO in an iron matrix are now complete. The bulk of these tests were carried out with an iron - 1.3 weight percent beryllium alloy. Most of the work had finally been concentrated on two preferred processes, namely:

- a) internal oxidation of powders at 650, 850, and 1000°C, using H_2O-H_2 ratios of 0.25 to 0.45.
- b) Complete oxidation at the same temperatures but with H_2O-H_2 ratios greater than unity. The totally oxidized powders were then subjected to selected reduction in dry hydrogen to reduce preferentially the iron oxide to iron, without affecting the BeO.

The BeO was extracted from the iron matrix for electron microscopy and X-ray diffraction studies. Extraction was by means of preferential dissolution of the alloy in a solution of 15% bromine in methanol. X-ray diffraction patterns showed only BeO in the residue. The resultant oxide particles appear to be considerably finer after internal oxidation as compared to total oxidation plus selective oxide reduction. Equally good results appear to have been produced by internal oxidation at 650 and 850°C, but more precise measurements will be made to optimize the temperature. The BeO particles are much too coarse after the 1000°C treatment.

Electron microscopy studies were carried out at magnifications from 10,000 to 68,000X. Internal oxidation at 650 and 850°C yielded irregular, but round cornered disc-shaped oxide plates. The long dimensions varied between 0.03 and 0.3 micron, the average size being in the range 0.10 to 0.15 micron. Thicknesses of the discs were of the order of 200 to 1500 Å, most being in the range 500 - 1000 Å. These particles are transparent to the electron beam. At 1000°C, the long dimensions of the particles were 4 to 5 times larger; however, the thickness did not increase appreciably at the higher temperature.

Complete oxidation of the iron-beryllium powders appeared to result in some agglomeration of BeO particles, leading to a considerably coarser structure after selective reduction.

Metallographic studies indicate that internal oxidation of the -44 micron alloy powders was essentially complete after about 24 hours at 1000°C, and was 75 - 90 percent complete in the same time at lower temperatures. Calculation of the oxidized zone penetrated at the 3 exposure temperatures to show penetration rates of 10^{-9} cm²/second at 1000°C,

$6 \times 10^{-11} \text{ cm}^2/\text{second}$ at 850°C , and $2 \times 10^{-12} \text{ cm}^2/\text{second}$ at 650°C . Based on these results, plus preliminary checks with the 0.5 weight percent beryllium-iron alloy, the preferred processing for production of bar stock will call for internal oxidation at $750\text{--}800^\circ\text{C}$ for about 40 - 48 hours, using $\text{H}_2\text{O}:\text{H}_2$ ratios of 0.3 - 0.4.

Chemical analysis and electron diffraction data indicate that a significant amount of surface iron oxide is formed on re-exposure of the fine powders to air after internal oxidation. This condition will have to be corrected by hydrogen reduction either during compaction, or during the canning procedure prior to extrusion. The presence of excess FeO in these alloys would lead to unstabilization of the BeO at the higher test temperatures.

Final comminution of the atomized iron-beryllium alloys is now well under way. The next three to four months will see production of alloys by the internal oxidation process, with considerable effort spent on creep and stress rupture testing. Using the highest beryllium containing alloy, tests will also be made using the SAP technique of producing a surface oxide of BeO, followed by reduction of any FeO, followed by canning and extrusion. This will produce an alloy in which some beryllium will remain in the iron matrix, coupled with a fine dispersion of BeO particles in the matrix.

C) Oxide Dispersion Strengthened Copper - Al_2O_3 Alloys by the SAP Technique

Electron microscopy examination of material comminuted by attrition for 6 hours in ethanol showed that the flake thickness of the resultant product was about 0.1 micron (totally transparent). As a result of this accomplishment, all the remaining alloys have been comminuted to fine flake product, with a long dimension of 3 to 5 microns and a thickness dimension of about 0.1 micron.

Approximately 5-pound lots of these ultra fine powders are now available, and will be processed in two different ways:

a) Reduction of any surface copper oxide. All the aluminum will not be oxidized by this technique and the matrix will contain aluminum.

b) Internal oxidation utilizing the surface copper oxide as a source of oxygen. All the aluminum should be oxidized, leaving a matrix of pure copper.

A large furnace has been modified to handle these powders according to the two indicated procedures.

Modifications have also been made in other equipment to protect the powders after reduction so that recontamination of the powders by oxygen will be avoided.

The studies of comminution by attrition have shown that the optimum amount of material in the one gallon attriter mill is two kilograms of -44 micron starting alloy. A grinding time of 6 hours appears to be sufficient to achieve the flake sizes desired. Ethanol has proven to be the best surfactant or grinding aid; the ethanol is readily removed from the fine copper flakes, leaving no residue.

The next three to four months should see the production of bar stock and the initial creep and stress rupture testing of the resultant alloys.

D) Chromium Oxide Control in Oxidation Resistant - Oxide Dispersion Strengthened Alloys

There are two schools of thought regarding the apparent lack of stability in oxide dispersion strengthened, oxidation resistant alloys. One school believes that the refractory oxide (ThO_2 , BeO , ZrO_2 , etc.) is unstabilized by the presence of copious amounts of chromium oxide. The high vapor pressure of chromium oxide leads to its ready dissociation, with subsequent reprecipitation on the refractory dispersed oxide, leading to coarsening and weakening. The second school suggests that chromium itself, even in the absence of excess oxygen, may be capable of partially reducing refractory oxides such as BeO , ThO_2 , Al_2O_3 , and others. Both arguments can be substantiated thermodynamically, but experimental evidence is needed to verify or refute these arguments.

In preliminary studies we have made a large number of diffusion couples between chromium and several chromium alloys, containing highly reactive solute elements, and solid thoria. These diffusion couples were exposed for 100 hours at 2000 and 2100°F. No evidence of interaction was observed in these crude, preliminary studies.

In the meantime, minus 10 micron powders have been obtained of alloys of both austenitic and ferritic stainless steel compositions. Specifically, alloys 310 and 316 have been obtained of the austenitic type, and type 440 has been obtained of the ferritic grade. These 10 micron powders, of unusually high purity, have been blended with thoria, compacts will be made and sintered to high density, using reducing atmospheres, and then sealed in mild steel cans and extruded. These alloys will be exposed for long periods of time at progressively higher temperatures above 1800°F to determine the amount of reaction taking place between chromium (or chromium oxide) and thoria.

Supplementing the above tests will be two small samples of thoria dispersion strengthened type 316 stainless steel which differ significantly in the amount of chromium oxide present. These samples are currently being exposed for several time periods at increasing temperatures above 1800°F to see the role played by chromium oxide.

E) Internal Oxidation of Dilute Nickel Base Alloys

At this point in the study, concentrating largely on the nickel-beryllium and nickel-aluminum alloys, detailed studies of structure are now almost complete. These studies include determination of oxide particle size as a function of the internal oxidation temperature, time at temperature, change in oxide particle size as a function of depth of penetration of oxide, change in morphology of the oxide with increasing depth of penetration,

and effect of solute (aluminum) concentration. Electron microscopy studies, including examination of extracted oxides, have been utilized. In this way it is hoped not only to optimize conditions of temperature, time and solute concentration, but also to determine maximum alloy powder size.

There have been difficulties in achieving high temperature strength values in nickel (by any oxide dispersing technique) comparable to those achieved with the systems Al-Al₂O₃ and Cu-Al₂O₃ (on a homologous temperature scale). It is the intent of this study to determine if the properties can be improved by improvements in the structure of the alloy (oxide particle size and spacing, coupled with adequate cold work). The program is nearing completion at this point.

II. THE SPLAT COOLING PROCESS FOR ALLOY DEVELOPMENT

A) Development of a Continuously Operating Atomization Unit

To produce fine metal powder in various particle size ranges directly from the melt, a continuous cycle, shock wave generator has been built and is under test. The working principle is described below.

A thin disc (8 inches diameter) is mounted on a high speed spindle. On the circumference of the disc are machined 60 slits which, when in the right position, let air flow from a nozzle through the wheel openings. The nozzle is of the converging - diverging type in order to obtain ultrasonic flow of the gas jet out the outlet side. This ultrasonic jet is "chopped" by the rotating disc. The speed of the disc can be varied from 0 to 25,000 rpm resulting in a frequency spectrum of gas bursts from audible to ultrasonic. When the nozzles are positioned correctly, the gas bursts take the form of high energy shock waves. The shock waves impinge on a small diameter stream of molten metal and disintegrate it into droplets. The droplets can be collected either on a quench plate (splat cooling), or after solidification in flight, or after quenching into a liquid medium (water, oil, etc.).

Presently work is in progress to balance the components of the equipment in order to increase its efficiency and to ascertain the range of powder sizes which can be produced.

B) New Inert Gas Atmosphere Splat Unit for Small Alloy Quantities

To handle the many alloy compositions to be prepared and tested, an additional splat cooling unit was built. Its design is based on the original shock wave gun design by Duwez et al; however, a number of modifications have been made.

The new unit is capable of melting alloys up to about 1250°C in an inert gas atmosphere in aluminum oxide or other refractory crucibles. A protective atmosphere is also maintained in the path of the atomized metal particles and over the substrate. Reactive alloys, such as Cu-Be, with up to 31 atomic percent Be have been splat-cooled without apparent oxidation.

Further, the time between melts has been decreased; splats can now be made in intervals of two minutes, using an efficient way of exchanging the plastic gas pressure diaphragm and electric valves.

C) Alloy Studies

1. Decomposition of supersaturated Al-Si alloys: The solid solubility of Si in Al can be increased from 1.6 atomic percent Si (at the eutectic temperature) to about 11 atomic percent Si (at room temperature) by employing the splat cooling method of rapid

quenching from the liquid state. Quenched foils of Al-Si alloys containing 1, 4, or 11 atomic percent Si were produced and subsequently aged on the electron microscope hot stage. Aging treatments were carried out in a temperature range from 70 - 450°C. Measurements of particle size as a function of temperature and time have been made.

Activation energies for the precipitation process were calculated from the measured time when the first precipitates appeared. These activation energies decrease with increasing silicon content; they will be compared with those obtained previously from X-ray measurements of the same precipitation process. Under the present experimental conditions, there was no precipitate-free zone along the grain boundaries.

2. Al-Cu, Al-Ni, and other binary systems: A concerted effort was initiated to test the metastable solubility in Al for a number of possible strengthening additions. Alloys were made in the Al-Cu, Al-Ni, Al-Mn, Al-Fe, Al-Co, Al-Pd, and Al-Ag systems; the composition range was typically from 1-10 atomic percent solute, except for Al-Ag, where an alloy with 37.5 atomic percent Ag was tested.

In all investigated systems, there is a significant increase of the solubility in Al; thus, for Al-Cu the solubility is raised from max. 2.5 atomic percent Cu at the eutectic temperature to greater than 9 atomic percent. For Al-Ni, where the solid solubility of Ni in Al is less than 0.03 atomic percent at 600°C, at equilibrium, metastable solid solutions with 5 atomic percent Ni were prepared, an increase by a factor of 150X. Strongly increased solubilities were also found in the remaining systems.

The next step in the work will be a determination of the maximum solubilities and lattice parameter changes, followed by a study of the decomposition process in selected systems.

3. Copper-base alloy systems: Cu-Si alloys in the copper-rich section of the Cu-Si system have been prepared and splat-quenched. This section of the phase diagram is very complex in equilibrium, and at least 6 intermediate phases exist. It was found that in splat-cooled alloys the high-temperature phases are preserved throughout, giving the following sequence of observed structures:

$\alpha\text{-Cu (f.c.c.)} \rightarrow \kappa\text{(h.c.p.)} \rightarrow \delta\text{(b.c.c.)}$, with increasing Si content.

The solid solubility of Si in Cu was not found to be significantly enlarged; however, the other alloy phases were shifted from their equilibrium compositions by several atomic percent. The effect of heat treatments on these metastable structures has not yet been studied.

Cu-Be - In this technically important diagram, there is a large $\alpha\text{-Cu'}$ solid solution range with a strongly retrograde solvus line. This is followed by the b.c.c. β phase, decomposing eutectoidally at 605°C.

Five splat-cooled alloys between 2 and 6 weight percent Be were investigated. Consistent with the findings for Cu-Si, they show no significant increase in the solubility of Be in α -Cu, but show a shift in the homogeneity range of β towards higher Cu contents. The precise extent of this shift is still under investigation.

Since this newly found extended β phase is metastable, it will be possible to decompose it by suitable heat treatments into α -Cu and β' (or other transition phases); a strengthening effect on the Cu matrix analogous to that in customary Cu-Be alloys can thus be expected.

Interesting observations have also been made on previously unobserved ordering in the splat-cooled β phase.

D) Preparation of Test Materials From Splat-Cooled Foils

Preliminary consolidating tests were made on a eutectic Pb-Sn alloy. Foils of this alloy could be produced by splat-cooling with an existing unit, and 5-10 grams of this alloy were prepared. The material was then compacted in a steel die under 16,000 psi force and finally extruded into a wire of .125 inch diameter. Tensile samples were cut from this wire and mounted in a constant strain-rate machine.

The first test made on this alloy after aging at room temperature for four weeks showed local elongations of about 300 percent, approaching the range of superplasticity observed for this alloy by Backofen, Avery, and others. It can thus be concluded that sound specimens can be made from splat-cooled Pb-Sn alloys. Attempts to similarly consolidate copper alloy splats will be made shortly.